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Polymer Opals as Novel Photonic Materials

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Abstract

Synthetic opals, based on self-assembled arrays of core-shell (bead/matrix) polymer microparticles, are a promising platform for next generation bulk-scale photonic structures, coatings, fibres and sensors. This perspective article highlights recent work in this area, ranging from characterization and application, to advances in more fundamental understanding of structural color effects. These advances include visco-elastically-tuned symmetry breaking, the observation of anisotropic optical scattering, and the study of polymer opals as an analogue to the intrinsically disordered, low refractive-index contrast systems associated with opals seen in nature.

Keywords; polymers, photonic crystals, structural color, thin-films, opals

INTRODUCTION

The novel use of soft nanomaterials in the design of photonic structures, with macroscale internal structural bulk-ordering, presents opportunities for a step-change away from the monolithic architectures which are currently relied upon. Photonic crystals, where periodic variations in refractive index create photonic "band-gaps", allow the development of structured materials with distinguishing optical properties (e.g. structural color), which are not accessible using dyes or pigments.

In recent work, a low-cost, industrial-scale technique to produce flexible opals has recently been developed using melting and shear-ordering of core/shell polymer nanoparticles.[1,2] This is in marked contrast to many previous strategies for constructing photonic crystals, which have relied upon top-down lithography[3] or solvent driven self-assembly of high and low refractive index components.[4] Even simple structures, such as photonic crystals *fcc* lattices, based on these methods cannot be fabricated in any scalable fashion, and the resultant structures notably lack any mechanical robustness. No precedents exist for the application of shear ordering techniques to these granular solvent-free systems, which allow formation of permanent, mechanically robust composites in the solid-state (figure 1). The resultant structures are low-defect flexible polymer *fcc* opals films, with fundamental optical resonances tunable across the visible and near-infrared regions (by varying the precursor particle size from 200-350 nm, and hence the resulting lattice parameter). In the lower refractive-index contrast regime associated with these polymer composites ($\Delta n \approx 0.1$), color generation arises through spectrally-resonant scattering inside a 3D *fcc*-lattice photonic crystal generating a "scattering cone",[5,6] as opposed to normal reflective iridescence based on Bragg diffraction. In addition, one of the most attractive features of elastomeric polymer opals is the tunability of their perceived color by the bending or stretch modification of the (111) plane spacing.

The fabrication technique employed uses shear-flow self-assembly of core-interlayer-shell (CIS) polymer particles into 3D cubic lattices through extrusion at high temperatures. As illustrated in Figure 1b, the core-shell particle precursors are typically 200-300 nm in diameter, and consist of a hard polystyrene (PS) core, coated with a thin polymethylmethacrylate (PMMA) "grafting" layer, and a soft polyethylacrylate (PEA) outer shell. These particles are prepared using a multi-stage emulsion polymerization process.[1] The material may be processed using a twin-screw mini-extruder and adjustable temperatures

of 25-250°C. Bulk quantities of the opal precursor materials (as shown in figure 1a) are manually driven into the extruder, where they form a melt and are homogenized under the extreme shear forces provided by recycling through the screws. The overpressure generated then drives the shear-ordered granular material through a narrow-bore stainless steel die, producing bulk opaline ribbons. In such polymer opal films, ordering proceeds from the outer flat surfaces which seed accumulation of (111) planes,[7] but recent work has now shown that it is also possible to produce opaline fibers by extrusion in a wire geometry.[8]

Additionally, the introduction of a small (~0.05% by weight) fraction of carbon nanoparticle pigment into the interstices of the photonic crystal lattice does not disrupt the lattice quality, but results in a remarkable increase in the color saturation of the opals with the concentration of carbon, as shown in figure 1e.[5] This principle is of fundamental interest in understanding the origins of structural colors and iridescence in natural opals, such as those in minerals or in biological structures.[9] However, the main difficulty of this fabrication approach has been the lack of true bulk order.

A significant advance was achieved with an edge-induced rotational shearing (EIRS) process, which produces reproducible highly uniform samples with bulk-ordering of sub-micrometer components, greatly enhancing both the intensity and chromaticity of the observed structural color.[10] A schematic of this mechanically controlled process and the associated optical properties are given in figure 1f. In brief, the process consists of a combination of bulk extrusion, followed by rolling (linear shear) into ~100 μm thick films, and finally edge-induced rotational shearing (across a polished metallic hot-edge, with an apex angle of $\alpha = 90°$ and radius of curvature < 10 μm) yielding permanent rolls of opaline film. As a powerful demonstration of the 3D bulk ordering achieved in these opaline films, optical diffraction experiments readily revealed very clear and distinctive diffraction-spot patterns, with a characteristic six-fold symmetry (figure 1d), which was precisely aligned to the processing direction in the EIRS process. Whilst the appearance of such well-resolved diffraction spots in transmission for the EIRS sample represents compelling evidence of crystallinity throughout the film of many hundred sphere layers, the appearance of six spots is also indicative of the presence of twinning and/or stacking faults within the cubic crystal structure.[11]

APPLICATIONS OF POLYMER OPALS

The demonstration of reproducible scale-up of these elastomeric synthetic opaline films to industrial length scales makes them very attractive as a route to a wide range of large-area photonics applications, including sensors and coatings. In this perspective article, we aim to summarize some of the most notable and promising examples, within the context of the underlying science.

In figure 2a, we see representative images of polymer opals with strong and vivid iridescence, as defined by the core-spacing and viewing angle. In addition to their subjectively decorative/aesthetic qualities, the unique structural color properties of polymeric opals, together with intrinsic processability, stretchability, and durability also potentially make them attractive for applications such as security or anti-forgery labeling, in banknotes, credit-cards and designer merchandise, for example. An illustration of how these favourable properties relate to applications is given in figure 2b, where a high-quality polymer opal film has been prepared as a novel textile, by attachment onto a fabric backing, using simple means of applying a cool iron-press. The sample shows all of the attractive properties of elastic stretch-, bend- and twist-tunability, in addition to a vivid structural color effect.[12]

As an extension of the polymer processing technologies reviewed here, extruding high-quality opaline fibers in an industrially-scalable fashion is now also practical (figure 2c).[13] As with the opaline thin-films, these fibers exhibit structural color based on the self-assembly of sub-micron core-shell particles, with a spectrum which is stretch-tunable across the visible region. Fibres are directly extruded by using modified circular dies of diameters ranging from 100-2000 μm. Since ordering during standard extrusion proceeds from the outer flat surfaces which seed accumulation of (111) planes, it was far from obvious that opal fibers could be produced.[7] However, in addition to experimental demonstration, a dynamic theoretical (granular) model predicts the formation of ordered close-packed layers on the outer region of the fiber, and the growth of this order inwards from these seed layers. In both experiment and theory, fibers are characterized by an internal substructure, in which a concentric zone near the exposed surface develops particularly strong structural color. After suitable UV-A photo-crosslinking, the final fiber products have sufficient mechanical robustness to allow them to be hand-knitted into stretchable fabrics. These elastically-tuned fibers are thus potential candidates for a novel range of nano-materials and clothing fabrics, utilizing strong structural color effects as a replacement for toxic and photodegradable dyes.

Large-scale shear-ordered photonic crystals have also been shown to exhibit unusual *thermochromic* properties.[14] By balancing the refractive index of the polymer core and composite shell components at room temperature, transparent films are created, which become coloured on heating (figure 2d). Since this scattering-based structural color depends only on resonant Bragg scattering of non-pigmented components, it can be tuned to any wavelength. Whilst it is expected that there is a thermally induced change in refractive index contrast, the observed color shifts with temperature are not accounted for by simple theory, and probably reflect a more complex interaction between the core and shell indices, and the mechanical expansion and strain effects upon heating. This thermochromic mechanism can also be harnessed in a wide variety of ways by tuning core and shell sizes and polymer compositions, pointing towards a potential use of such opals in thermal sensors and indicators, where large areas may be important (e.g. food packaging). Further optimization and incorporation of other (e.g. emissive) nanoparticles would also open a range of potential applications in displays and in switchable structural color materials.[15]

The prospects for utilizing such photonic materials in optoelectronic applications, such as photovoltaics or electrically tunable colour films, require conductive colloidal crystals which have been unavailable thus far. In the recent work of Imai *et al*.,[16] electrically conductive polymeric 3D photonic crystals are prepared by the shear ordering of hetero-coagulated composites consisting of monodisperse core-shell polymer spheres and single-walled carbon nanotubes (SWNTs). The retention of strong iridescent color indicates that the highly ordered polymer opal structures are not disrupted by the presence of the conductive nanotube networks. Thermal annealing leads to a significant increase in the overall electrical conductivity of thin-film samples yielding DC conductivities of 10^{-4} S cm^{-1}, with percolation thresholds of less than 0.4 wt% of SWNT. As well as this work being an important milestone in the quest for "conductive photonics", it is anticipated that further optimization of processing parameters, such as those of the sample annealing, will enable yet higher conductivities to be reached, making further practical applications feasible. Following on from Imai *et al*., electrically tuned photonic crystals have also been demonstrated by applying fields across shear-assembled elastomeric polymer opal thin films.[17] At increasing applied electric-fields, the polymer opal films stretch biaxially under Maxwell stress, deforming the nanostructure and producing marked color changes. This electro-optic tuning of the photonic bandgap is rapid (switching at < 100 ms), and repeatable over many cycles, bridging the gap between electro-active materials and photonic crystals.

A PLATFORM FOR EXPLORING THE FUNDAMENTAL PHYSICS OF PHOTONIC CRYSTALS AND STRUCTURAL COLOR

Besides the technological applications of polymer opals, such systems are interesting analogues of structural color in nature, as well as the intensity of scatter from clouds and radar imaging. Additionally, the durable visco-elastic properties of the samples allow access to a whole host of experiments, and the associated scientific insights, which are mechanically impossible in more conventional monolithic photonic crystals.

Symmetry is a crucial ingredient in the self-assembly of nanostructures with novel optical, electronic, magnetic or thermal functionality. However many new physical properties that are desirable to access, depend on breaking this symmetry to introduce higher-order complexity, which has proved difficult.[18] Polymer opals have been used as a paradigm to demonstrate elastically induced phase transitions to break the structural symmetry of self-assembled nanostructures, producing significantly modified functional properties. Stretching ordered polymer opals in different directions transforms the *fcc* photonic crystal into correspondingly distorted monoclinic lattices. This breaks the conventional selection rules for scattering from the crystal planes, yielding extra multiply scattered colors when the phase-breaking stretch is in specific directions. Scattering has been spectroscopically tracked in real time as the samples distort, revealing a new phase transition into a lower symmetry monoclinic lattice structure.[19] New, normally-forbidden Bragg peaks become immediately visible (as the condition for *fcc* that Miller indices *h*,*k*,*l* must be all even or all odd is broken); such effects have not even been experimentally observed in atomic crystals.

Photonic properties have also been widely studied in natural biomaterials which self-assemble in more sophisticated ways,[20] such as butterfly wings, beetle carapaces, and flower petals. However, such self-assembly processes intrinsically incorporate disorder in the nanostructures, which degrades the reflectivity but enhances the wider scattering of light (i.e. into “scattering cones”). In that sense, polymer opals represent an important analogue by which a full understanding of the role of such disorder in the optics are such systems may be characterized. Recently, hyperspectral goniometry has been used with a polymer opal sample to demonstrate how to completely reconstruct the reciprocal space of scattering vectors.[21] This yields the three dimensional shape of the dominant reciprocal-lattice point responsible for the intense structural color, and separates resonant and background scattering processes. In these crystals, a previously unknown but significant anisotropy of the scattering process

which dominates the optical interactions, was identified. Such measurements yield a composite image at each incident wavelength (figure 3a) which captures the front surface specular reflection peak while clearly resolving the resonant-scattering cone (which is up to two orders of magnitude less intense). Analysis reveals that the scattering is anisotropic in all three directions, appearing as a flattened ellipsoid. While an anisotropic response to stress has been previously reported (described above), this *optical* anisotropy is intrinsic to the nanostructure, appearing in all unstretched samples. This anisotropy has origins in the directionalized ordering of the EIRS process and it was found that short chain defects govern the observed angular scattering cone. This implies that defects spatially localize light over length scales of many sphere periods, and their control thus plays a crucial role in self-assembly of structurally colored photonic crystals.

The refractive index contrast (Δn) between the core beads and the matrix polymer is essential for the appearance of such structural color; however, it is not clear how the strength of such resonances changes as Δn increases. The index contrast between core and shell materials can be varied by controlling the chemical composition of the shell material using low refractive-index fluorinated monomers[22] (figure 3b, inset).[23] The effect of Δn, on the resonant scattering and reflectivity of polymer opals, within a regime of $\Delta n < 0.2$ has been recently studied. The strength of resonant Bragg reflection from polymer opals is found to vary linearly with the refractive-index contrast, Δn, in marked contrast to the expected quadratic buildup of Fresnel reflections scaling as $(\Delta n)^2$. This occurs due to the interplay of disorder and periodicity, in close agreement with a simple 1-dimensional periodic model with inbuilt disorder, as shown in figure 3b.[24] Hence, the degree of disorder in the sample demonstrably plays a fundamental role in these linear dependencies. In previous studies of polymer opals, we presented crystallographic evidence of stacking faults and/or twinning within the cubic structures, which introduces a certain level of disorder throughout the films. It is likely that these characteristics are also intrinsic to many self-assembled periodic structures, including those found in nature.[9,20,25]

SUMMARY

Elastomeric polymer opals, in both thin-film and fibre form, can now be manufactured using ubiquitous polymer processing techniques and have many attractive functional features; intense structural color, with inherent stretch- and bend-tunability, and excellent durability and mechanical robustness. As demonstrated, these opals are thus potential candidates for a novel range of nano-materials, coatings, sensors, and also clothing fabrics, utilizing structural color effects as a replacement for toxic and photodegradable dyes.

In addition to these innovative applications, polymer opals have also proved to be a highly fruitful platform for more fundamental experimental studies of the physics of photonic crystals, structural color, and of the self-assembled optical structures seen in Nature. In particular, practical demonstrations of symmetry breaking in photonic crystals, and a deeper understanding of the roles of disorder, anisotropy and index-contrast in structural color, have been achieved. We anticipate further developments in this regard in the future, and the extension of the archetypal core-shell polymer opal system, into a yet wider range of engineered functionalities and applications, including novel biomimetic strategies.

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FIGURES

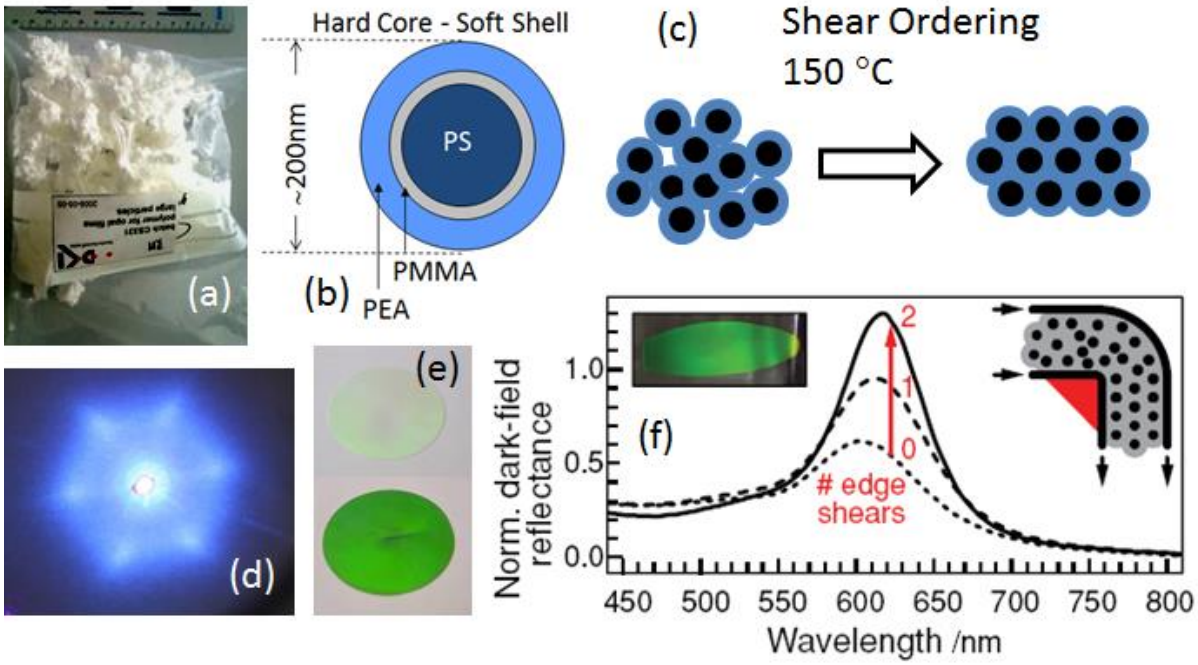

Figure 1; (a) A bulk batch of as-synthesized core-interlayer-shell (CIS) particles, used for polymer opal production. (b) Schematic of the CIS system, based on polystyrene(PS)-polymethylmethacrylate(PMMA)-polyethylacrylate(PEA). (c) Schematic of the fabrication technique using shear-flow self-assembly of polymer particles into 3D cubic lattices at high temperatures. (d) Transmission diffraction pattern taken at normal incidence for a ≈ 40 μm thick film of an edge-sheared opal with sphere diameter of 630 nm. (e) Green polymer opal films showing the large enhancement of structural color saturation with the addition of 0.05% by weight of carbon nanoparticles. (f) Dark-field spectra of polymer-opal films show improving order with edge shearing. Data are normalized to a reference Lambertian scatterer. The insets show a photo of an edge-sheared polymer-opal film (≈ 6×2 cm, left), and edge-induced rotational shear processing of core-shell nanospheres between rigid PET tapes (right).

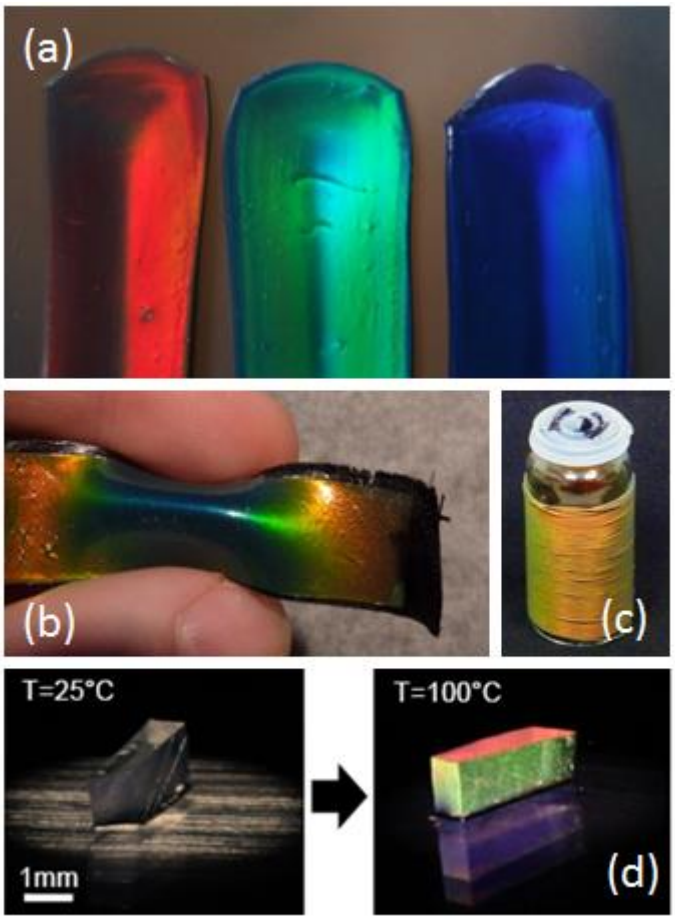

Figure 2; (a) Illustration of the striking iridescence of red, green and blue polymer opal thin-films. Core particle sizes range from ~300 nm (red) to ~200 nm (blue). (b) A polymer opal mounted onto a Lycra fabric, illustrating the stretch-, bend-, and twist-tunability. (c) Post-extruded long fibers of opaline quality. (d) Images of the change in an iso-refractive opal structure as the temperature is raised, illustrating a clear thermochromic effect.

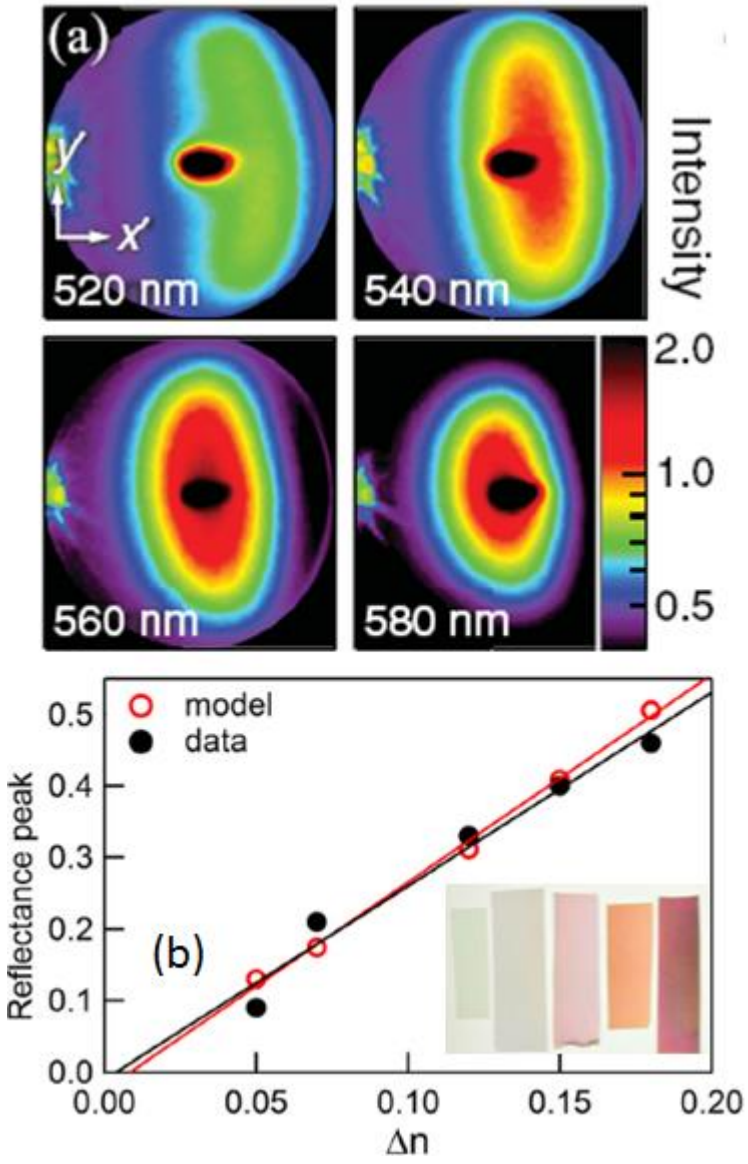

Figure 3; (a) Intensity pattern of scattered light from a polymer opal at various wavelengths, as projected onto a hemispherical screen, showing highly anisotropic scattering (images use a high dynamic range false color scale as indicated). The small black spot in the center is the intense specular reflection; the hole through which white-light is introduced is seen on the left. (b) Normal incidence reflectance peak heights plotted as a function of index contrast, Δn, with linear fits to both experimental data and a 1D multilayer quasi-model. In the model, layers had an inbuilt disorder of 7% of the interlayer thickness. The inset shows the samples (widths of ~3cm) as viewed in transmitted white light, with the index contrast increasing from left to right.

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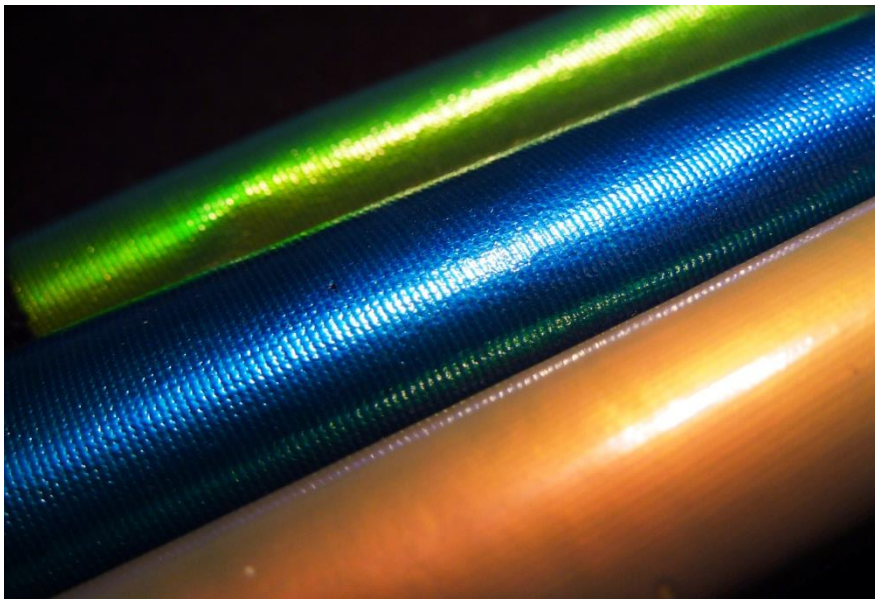

Caption; Synthetic opals, based on self-assembled arrays of core-shell polymer composite microparticles, are a promising platform for next generation bulk-scale photonic structures, coatings and sensors. Additionally, such medium contrast photonic crystals are of importance for a more fundamental understanding of the phenomenon of structural color.